ABSTRACT

India, like most of the developing countries of the world, despite its potential agricultural resources, is still highly dependent on imported crude oil for energy production. With its growing population, India’s present demand for the energy is 3.5% of world’s energy demand and is expected to grow at the rate of 4.8% per annum. As the demand of crude oil has increased dramatically and thus, country’s cost for the import of crude oil has increased substantially. Diesel fuels play an important role in the industrial economy of a country. These fuels run a major part of the transport sector and their consumption is increasing steadily. The intensity of fuel consumption is directly proportional to a society’s development. Diesel fuels, in India are used in heavy trucks, city transport buses, locomotives, electric generators, farm equipments, underground mine equipments, etc. Today, more and more developing countries are prospering through economic reforms and are becoming industrially advanced.

But, the use of fossil fuels is one of the major sources of world wide environmental pollution, the green house effect and acidification of both soil and water. The high energy demand in the industrialized world and pollution problems caused due to widespread use of fossil fuels make it necessary to develop the renewable energy sources of limitless duration and smaller environmental impact than the traditional one.

Mainstream forms of renewable energy include wind power, hydropower, solar energy, biomass, and biofuels. Airflows can be used to run wind turbines. Modern wind turbines range from around 600 kW to 5 MW of rated power, although turbines with rated output of 1.5–3 MW have become the most common for commercial use. Energy in water can be harnessed and used. Solar energy is the energy derived from the sun through the form of solar radiation. Solar powered electrical generation relies on photovoltaics and heat engines. A partial list of other solar applications includes space heating and cooling through solar architecture, day-lighting, solar hot water, solar cooking, and high temperature process heat for industrial purposes. Biomass is a renewable energy source because the energy it contains comes from the sun. Through the process of
photosynthesis, plants capture the sun's energy. When the plants are burned, they release the sun's energy they contain. In this way, biomass functions as a sort of natural battery for storing solar energy. As long as biomass is produced sustainably, with only as much used as is grown, the battery will last indefinitely.

Number of researchers have investigated for alternate fuel sources and concluded that vegetable oil based fuels can also be used as alternative fuels. The majority of Asian countries are net importer of edible oils; therefore these oils cannot be used for the production of biodiesel. In South Asian countries like India, biodiesel can be harvested and sourced from non-edible seed oils like jatropha and pongamia. For example, Jatropha curcas is such a tree which can grow on any type of soil, needs minimum input and management, has low moisture demand, starts giving seeds after third year of plantation, has 25–30% oil content and productive life is more than 40 years. In fact, implementation of biodiesel in India will lead to many advantages like providing green cover to wasteland, support to agricultural and rural economy, and reduction in dependency on imported crude oil and reduction in air pollution. The seed mass after extraction of oil has a very good nutritious value as fertilizer and therefore, will add a very large amount to the fertilizer pool resulting in reduction in subsidies and rejuvenation of wasteland.

According to proposed National Mission on biodiesel in India, we have undertaken studies on the physico-chemical properties of biodiesel from tree borne non-edible oil seeds J. curcas and Pongamia pinnata. Physico-chemical properties of palm biodiesel (PBD) synthesized from palm oil were also investigated. Research was conducted to investigate the influence of presence of transition metals, likely to be present in the metallurgy of storage tanks and barrels; on the oxidation stability (OS) and physico-chemical properties of biodiesel. Influence of the organic contaminants like vegetable oils, free fatty acids and glycerol likely to be present in biodiesel; on the OS and physico-chemical properties of biodiesel were also investigated. Further, research was conducted to establish the correlations between various physico-chemical properties of biodiesel with fatty acid methyl ester (FAME) composition. To minimize the use of biodiesels synthesized from edible oils like palm due to raising food versus fuel issue,
PBD was blended in different weight ratios with biodiesels synthesized from tree borne non edible oil seeds jatropha, and pongamia to examine the effects on OS and low temperature flow properties of biodiesel.

The main problem with vegetable oil is that it is much more viscous than commercial diesel fuel. The high viscosity of raw vegetable oil reduces fuel atomization and increases penetration thought to be partially responsible for engine deposits, piston ring sticking, injector coking and thickening of oil, however, these effects can be reduced through transesterification of the vegetable oil to form monoesters which reduce viscosity. These monoesters are known as biodiesel. Thus, technically speaking, biodiesel is the alkyl ester of fatty acids, made by the transesterification of oils or fats, from plants or animals, with short chain alcohols such as methanol and ethanol in the presence of catalyst and glycerin is consequently a by-product from biodiesel production.

Therefore, first objective of the research was to prepare the biodiesel by transesterification process to reduce viscosity. Biodiesel was prepared by transesterification process, involving reaction of oil with methanol under reflux conditions. A series of experiments were used to design to determine the optimal reaction conditions to get maximum conversion. Methanol (8:1 M ratio to oil) was added to the reactor followed by slow addition of catalyst (0.6 wt% of oil) with stirring. The stirring was continued until the complete dissolution of catalyst (15 min). To the stirred solution, oil was added and the reaction temperature was set at 65°C for the experiment. After completion of the reaction the material was transferred to separating funnel and both the phases were separated. Upper phase was methyl ester (biodiesel) and lower part was glycerin. Alcohol from both the phases was distilled off under vacuum. The glycerin phase was neutralized with acid and stored as crude glycerin. Methyl ester was washed with the water twice to remove the traces of glycerin, unreacted catalyst and soap formed during the transesterification. The residual product was kept under vacuum to get rid of residual moisture.

Biodiesel samples were tested for physico-chemical properties as per Indian standard IS-15607, American standard test method ASTM D-6751 and European EN-14214 standards. Subsequent analysis showed no statistically significant difference
between the measurements. The biodiesel standards IS-15607 and EN-14214 call for determining oxidative stability at 110°C with a minimum IP of 6h by the Rancimat method (EN- 14112). Even ASTM standard D-6751 has recently introduced a minimum IP of 3h. Jatropha biodiesel (JBD) meet all the specifications, except induction period (IP) of 6h. Neat pongamia biodiesel (PoBD) showed the IP of 2.54h so did not meet the minimum limit of 3h IP in accordance with recent ASTM D-6751 and minimum limit of 6h IP as required by EN-14112 standards. In the Rancimat Method, the oxidation was induced by passing a stream of air at the rate of 10L/h through the biodiesel sample, kept at constant temperature 110°C. The vapors released during the oxidation process, together with the air, were passed into the flask containing 50mL of demineralized water, and contain an electrode for measuring the conductivity. The electrode is connected to a measuring and recording device. It indicated the end of IP when the conductivity began to increase rapidly. This accelerated increase was caused by the dissociation of volatile carboxylic acids produced during the oxidation process and absorbed in the water. When the conductivity of this measuring solution was recorded continuously, an oxidation curve is obtained whose point of inflection is known as the IP. Oxidative rancidity begins with an initial chain reaction:

\[ RH \rightarrow R' \]

followed by a propagating reaction that involves unstable peroxides and hydroperoxides:

\[ R' + O \rightarrow ROO' \]

\[ ROO' + RH \rightarrow R—OOH + R' \]

followed by the termination reactions resulting in aldehydes, alcohols and carbonic acids:

\[ R' + R' \rightarrow R—R \]

\[ ROO' + R' \rightarrow R—O—O—R \]

PBD satisfy the aforementioned specifications of OS. Neat PBD exhibited an OS of 9.24h; thus it is highly stable but exhibited poor low temperature flow properties. The low temperature flow properties of biodiesel are characterized by cloud point (CP), pour point (PP) and cold filter plugging point (CFPP) and these must be considered when operating compression-ignition engines in moderate temperature climate during winter months. “CP” is the temperature at which a sample of the fuel starts to appear cloudy,
indicating that wax crystals have begun to form which can clog fuel lines and filters in a vehicle’s fuel system, “PP” is the temperature below which the fuel will not flow and “CFPP” is the temperature at which fuel causes a filter to plug due to its crystallization. CP and PP were measured according to ASTM D-6751 test methods ASTM D2500, D97 respectively and IS: 1448 P: 10. CFPP was measured according to ASTM D-6371, EN-116 and, IS: 1448 P: 10. High CP and PP values of biodiesel can be explained by high contents of the saturated fatty acid alkyl esters because the unsaturated fatty acid alkyl esters have lower melting points than the saturated fatty acid alkyl esters.

FAME composition of biodiesel samples were determined by gas chromatography on a gas chromatograph (GC). FAME composition of jatropha and pongamia biodiesel samples showed that these samples mainly consisted of unsaturated fatty acid methyl esters like oleic and linoleic fatty acid methyl esters. The contents of saturated fatty acids methyl esters for palm, jatropha, and pongamia biodiesels were 44.4, 21.1, and 16.0% respectively and the contents of unsaturated fatty acids methyl esters for three biodiesels were 55.6, 78.9, and 84.0% respectively. Therefore, jatropha and pongamia mainly consisted of unsaturated fatty acid methyl esters and palm consisted of approximately equal concentrations of saturation and unsaturation. Low OS and good low temperature flow properties of jatropha and pongamia can also be attributed due to more unsaturation.

Further, tests were done to improve the low OS of jatropha and pongamia biodiesels by doping different antioxidants with varying concentrations. Synthetic antioxidants namely tert-butylated hydroxytoluene (TBHT), tert-butylated phenol derivative (TBP), octylated butylated diphenyl amine (OBPA), and tert-butylhydroxquinone (TBHQ) and natural antioxidant α-tocopherol (α-T) were selected for this purpose. All the antioxidants were doped to the biodiesel samples with varying concentrations (ppm), and corresponding IPs were measured with the Rancimat test method to observe the effectiveness of different antioxidants. Synthetic antioxidants showed better antioxidant property than natural antioxidant. When compared all antioxidants, TBHQ was most effective in enhancing the IP of JBD. The antioxidant property of TBHQ is greater than other antioxidants investigated. This can be explained based on their molecular structures, which the former possesses two OH groups attached
to the aromatic ring and thus, TBHQ offers more sites for the formation of complex between free radical and AO radical for lipid stabilization purpose.

Research was conducted to investigate the effect of presence of transition metals-iron, nickel, manganese, cobalt, and copper, likely to be present in the metallurgy of storage tanks and barrels, on the OS of biodiesel samples. Different transition metals were blended with varying concentrations (ppm) in biodiesel samples. It was found that influence of the metals were detrimental to OS and catalytic, as even small concentrations of metal contaminants showed nearly the same influence on OS as large amounts. Copper showed the strongest detrimental and catalytic effect on OS. Neat PBD exhibited an OS of 9.24h; thus it is highly stable and it was found that influence of metal was detrimental and catalytic even for stable palm. The presence of metals in biodiesel resulted in acceleration of free radical oxidation due to a metal-mediated initiation reaction and strongest catalytic effect of copper is due to its relative higher pro-oxidant effect.

The OS of metal-contaminated palm methyl ester (PME) was found to increase with increases in dosage of antioxidants. It was found that antioxidant TBHQ is most effective among all the antioxidants used. The OS of metal-contaminated biodiesel was found to increase with increase in dosage of antioxidant but dosage required for copper-contaminated biodiesel sample became approximately four times than required for neat biodiesel sample to meet EN-14112 specification for biodiesel OS.

It was found possible to meet the desired EN specification for the OS for neat biodiesel and metal-contaminated biodiesel by using antioxidants; it will have a cost implication, as antioxidants are costly chemicals. Research was conducted to increase the OS of metal- contaminated biodiesel by doping metal deactivator with antioxidant, with varying concentrations in order to meet the aforementioned standard required for the OS. It was found that usage of the antioxidant can be reduced by 30 – 50%, therefore the cost, even if very small amount of metal deactivator is doped in biodiesel to meet EN-14112 specification.

Effect of the minor contaminants like monoglycerides on the biodiesel physicochemical properties was also investigated. These contaminants may be present in the crude oil and be carried through after incomplete conversion during transesterification
and processing of the biodiesel product. Monoglycerides were measured according to EN ISO 14105 method and water is measured according to D-2709 methods of ASTM and Indian standards. Water is a major source of fuel contamination. While fuel leaving a production facility may be virtually water-free, once it enters the existing distribution and storage network, it will come into contact with water. Water typically enters fuel tanks through vents and seals as humidity in the air. The water condenses or is dissolved into the fuel. Virtually all diesel fuel storage tanks can be assumed to contain some water.

Water in the fuel generally causes two problems. First, it can cause corrosion of engine fuel system components. The most direct form of corrosion is rust, but water can become acidic with time and the resulting acid corrosion can attack fuel storage tanks. Therefore, the effect of monoglycerides, water and soap contamination, on the biodiesel properties was investigated. It was seen that increase in levels of these minor contaminants has negative effect on the low temperature flow properties of biodiesel. These contaminants have minor effect on the stability of JBD. JBD has OS of 3.95h, the blends of these contaminants at different levels only decreases the OS to 3.26h.

Palm, jatropha, and pongamia biodiesels used in this work had CPs of 16.0, 4.0, and -1.0°C, PPs of 12.0, -3.0, and -6.0°C and CFPPs of 14, 1, and -2°C respectively. Therefore, palm had very poor low temperature flow properties. To minimize the use of biodiesels synthesized from edible oils like palm due to raising food versus fuel issue, PBD was blended with different weight ratios (%) with biodiesels derived from tree-borne non-edible oil seeds jatropha, and pongamia to examine the effect on CP, PP and CFPP of PBD. Blending PBD synthesized from edible oil with jatropha and pongamia biodiesel respectively, and with both, jatropha and pongamia biodiesels remarkably improved the CP, PP, and CFPP of PBD, so its use can be minimized.

Properties of various individual fatty esters that comprise biodiesel determine the overall fuel properties of the biodiesel fuel and in turn, the properties of various fatty esters are determined by the structural features of the fatty acid that comprise a fatty ester. The next objective of the study was to investigate the effect of the FAMEs compositions in the blended biodiesels on CP, PP, and CFPP and to determine the correlation between them. A good correlation between CP and palmitic acid methyl ester
(PAME) was obtained as \( CP = 0.526(PAME) - 4.992 \) \((0 < PAME < 45)\). For this equation, coefficient of correlation \((R)\) was 0.981, coefficient of determination \((R^2)\) was 0.963 and standard error of estimate \((\sigma_{est})\) was 0.929. A high degree of correlation between PP and PAME was obtained as \( PP = 0.571(PAME) - 12.240 \) \((0 < PAME < 45)\). For this equation, \( R = 0.929, R^2 = 0.863 \) and \( \sigma_{est} = 2.039 \).

The correlation between CP and total unsaturated fatty acid methyl ester (X) was also obtained as \( CP = -0.576(X) + 48.255 \) \((0 < X \leq 84)\). For this equation, \( R = 0.986, R^2 = 0.973 \) and \( \sigma_{est} = 0.788 \). The correlation between PP and X was \( PP = -0.626(X) + 45.594 \) \((0 < X \leq 84)\). For this equation, \( R = 0.935, R^2 = 0.874 \) and \( \sigma_{est} = 1.955 \).

A good correlation was also obtained between CFPP and contents of PAME (wt%) of three biodiesel blends as follows; \( CFPP = 0.511(PAME) - 7.823 \) \((0 < PAME < 45)\). For this equation, \( R = 0.929, R^2 = 0.863 \) and \( \sigma_{est} = 1.831 \). A good correlation was obtained between CFPP and X of three biodiesel blends as follows; \( CFPP = -0.561(X) + 43.967 \) \((0 < X \leq 84)\). For this equation, \( R = 0.934, R^2 = 0.872 \) and \( \sigma_{est} = 1.762 \).

The aforementioned results showed that with regard to the effects of the individual unsaturated fatty acid methyl ester, the good correlation could not be found. However, when the effects of total unsaturated fatty acid methyl esters were determined, a good correlation was found.

Using these correlations, cloud, pour and cold filter plugging points of different biodiesel blends can be determined. Therefore, to improve the poor biodiesel low temperature flow properties, blending of biodiesels over two is a simple but effective method and also it can minimize the use of edible oils. With the help of correlations between biodiesel low temperature flow properties and the FAME compositions, the low temperature flow properties of biodiesels produced from new resources can be easily estimated.

Similarly, dependence of OS on esters of fatty acid composition was also examined. Good correlation between OS and PAME was obtained as \( OS = 0.214(PAME) + 0.671 \) \((0 < PAME < 45)\). For this equation, \( R = 0.997, R^2 = 0.994 \) and \( \sigma_{est} = 1.762 \).
A correlation between OS and X was also obtained as 

\[ \text{OS} = -0.234(X) + 22.318 \quad (0 < X \leq 84) \]

For this equation, \( R = 0.999 \), \( R^2 = 0.998 \) and \( \sigma_{\text{est}} = 0.091 \).

Using the above correlations, cloud, pour and cold filter plugging points of different biodiesel blends can be determined. Therefore, to improve the poor biodiesel low temperature flow properties, blending of biodiesels over two is a simple but effective method and also it can minimize the use of edible oils. With the help of correlations, the low temperature flow properties and OS of biodiesels produced from new resources can be easily estimated.

From the present research, it can be concluded that it will not be possible to use biodiesel having low OS, poor physico-chemical properties like CP, PP and CFPP. The effect of presence of transition metals, likely to be present in the metallurgy of storage tanks and barrels, was detrimental to OS and catalytic. The stability of biodiesel is very critical and biodiesel requires antioxidant to meet storage requirements and to ensure fuel quality at all points along the distribution chain. Synthetic antioxidants are more effective than the natural antioxidants in increasing the OS of neat and metal-contaminated biodiesel. It was also investigated that the usage of antioxidant can be reduced, therefore the cost, even if very small amount of metal deactivator is doped in metal-contaminated biodiesel to meet EN-14112 specification. The dependence of the OS on the type of metal showed that long-term storage tests in different types of metal containers for examining the influence of container material on OS of biodiesel may be replaced by the significantly faster Rancimat test serving as an accelerated storage test. Organic contaminants likely to be present in the crude oil and be carried through after incomplete conversion during transesterification and processing of the biodiesel product also affected the low temperature flow properties, viscosity and flash point.

The production of biofuel from edible oils has raised serious concerns on preserving the food security of the planet and therefore, more emphasize should be given on biodiesel derived from tree borne non-edible oil seeds due to rising food-fuel issues. In this direction, it was determined that blending biodiesel synthesized from edible oil with jatropha and pongamia biodiesel respectively, and with both, jatropha and pongamia biodiesels remarkably improved the CP, PP, and CFPP of biodiesel from edible oil, so its
use can be minimized. With the help of correlations, between FAME compositions and low temperature flow properties and OS, the aforementioned properties of biodiesels produced from new resources can be easily estimated. Last but not the least, a carefully planned and executed national biodiesel program could provide energy security to India and at same time uplift the rural economy.